Analysis of the Charge/Discharge Behavior of Silicon Anodes

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There has been great interest in recent years on the use of alloy anodes, like silicon, in lithium-ion systems as a substitute for graphite. This interest stems from the large capacity of the silicon electrode (3579 mAh/g) when compared to graphite (372 mAh/g).[1,2] When used in a battery, this high capacity results in a significant increase in the energy density and specific energy of the cell (~25 to 30%). However, the large 1st cycle capacity loss, continuous side reactions during cycling, and the large volume change (270%) have all been detrimental to the commercialization of this system.[3]

In addition to these three issues, all silicon electrodes exhibit a voltage offset between lithiation and delithiation with the difference in potential being as high as 320 mV. This offset appears to be inherent to silicon whether it is made in composite,[2] nanowire[4] or a thin film form.[5] However, interestingly, literature data shows that silicon electrodes do exhibit reasonable rate capability, despite the hysteresis. This unique behavior has similarities to the behavior of other alloys and to conversion materials (e.g., NiP_2).[6]

The practical implications of this offset are twofold. First, the round-trip energy efficiency of a battery made with a silicon anode would be as low as 91%, even under very low rates. Note that in typical batteries, at low rates, one expects close to 100% energy efficiency, with the efficiency going lower at high rates due to ohmic, kinetic, and mass transfer limitations. Second, such an offset is a clear evidence of hysteresis wherein the state-of-charge (SOC) of the electrode is not clearly connected to the voltage of the system. In applications, such as hybrid-electric vehicles, these two aspects impact the use of this electrode in significant ways.

In this talk we will provide insights into the cycling behavior of silicon, pertaining to the offset, using thin films sputtered using a pulsed laser deposition technique along with a mathematical model. We have used these thin-film materials as a model system to understand the charge/discharge behavior of this anode and to provide insight into their operation under HEV cycling conditions.

The electrochemical behavior of this system is indicative of a system that is kinetically limited, similar to the carbon monofluoride system, studied recently.[7] What this means is that although the offset occurs even at low rates, as the rate is increased, no further kinetic penalty need be paid, indicative that high rates can be achieved.

Using open-circuit relaxation data on the thin-film anodes, we have estimated the kinetic parameters that control this behavior. We have then used these parameters to simulate constant-current operation using a mathematical model that incorporates a main reaction along with double-layer charging. Comparison of the model to experimental data shows excellent fits, although certain effects are not well described.

The model was then used to calculate the changes needed to remove the offset in potential and thereby increase the energy efficiency of the cell. This is captured in Figure 1 below where the offset potential and the energy efficiency is plotted against the dimensionless ratio, I/aLi_0, which captures the kinetic resistance of the system. Here I is the applied current density, a the interfacial area per unit volume, L the thickness of the electrode and i_o the exchange current density of the lithiation/delithiation reaction. A cathode potential of 3.8 V is assumed to estimate the energy efficiency.

The plot shows that removing the offset necessitates changes to the ratio I/aLi_0 by many orders of magnitude. While this can be achieved by making the particle size very small (thereby increasing the area), the large surface area would also result in a large amount of SEI formation and 1st cycle loss. The graph suggests that the offset in potential may be unavoidable unless a means is found to make the reaction more facile. Note that as the current density increases (i.e., ratio increases) ohmic and mass transfer effects, not captured in the plot, would play a greater role and the offset would show an increase.

This talk will discuss the experimental data on the behavior of the offset, the extraction of the kinetic parameters, its use in the mathematical model, and the predictive capability of the model. Insight will be provided into the behavior of this electrode when used in HEV applications, as it pertains to the offset.

References

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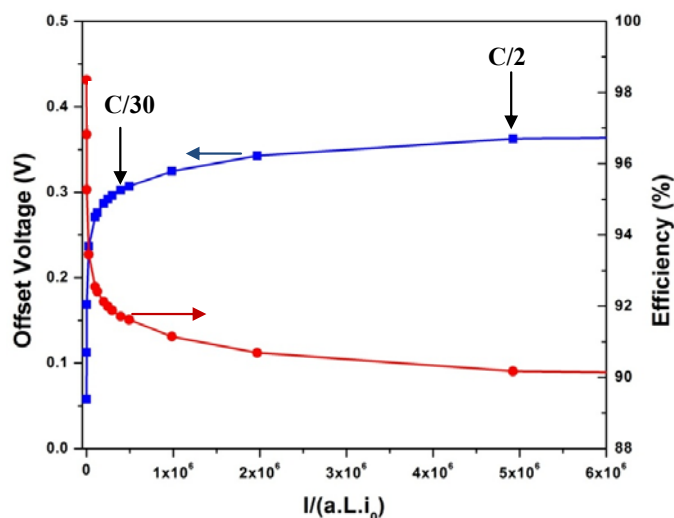7. S. Davis *et al.*, *J. Electrochem. Soc.,* **154**, A477 (2007).

Figure 1. Offset voltage and energy efficiency as a function of the controlling dimensionless ratio that captures the kinetic limitations in silicon.